Autoxydatie van additieprodukten van thiolen aan acetyleenethers

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SUMMARY

Chapter I* is devoted to the addition of thiols (RSH with R = ethyl, propyl, tert.butyl, benzyl, phenyl and p-tolyl) to ethoxyethyne.

In additions proceeding by a *free-radical* mechanism which could be inhibited by the addition of various inhibitors, the RS-residue became attached to the β-carbon atom of ethoxyethyne. A chain reaction was proposed:

$$C_2H_5O\underset{\alpha}{-}C\equiv\underset{\beta}{C}H + RS\cdot \rightarrow C_2H_5O-C=CH-SR \xrightarrow{RSH} \rightarrow C_2H_5O-CH=CH-SR + RS\cdot$$

The primary product probably had the *cis* configuration (*trans* addition). On distillation isomerisation occurred in the vapour phase so that mixtures of *cis* and *trans* isomers were obtained as was apparent from infrared absorption spectra. Addition of a second thiol molecule gave $C_2H_5SCH_2CH(OC_2H_5)SC_2H_5$ (for C_2H_5SH).

The *nucleophilic addition* of NaSR to ethoxyethyne produced I as was expected from the polarisation of the ethoxyethyne molecule:

$$H-\underset{\delta-}{C}\equiv\underset{\delta+}{C}-OC_2H_5 \xrightarrow{C_2H_5SNa} \underset{\text{I}}{CH_2=C(OC_2H_5)(SR)}$$

These nucleophilic additions were achieved in liquid ammonia or in super dry ethanol (for C_2H_5SH and p-$CH_3C_6H_4SH$). The ethoxyethyne was sometimes prepared *in situ* from chloroacetaldehyde diethylacetal or β-chlorovinyl ethyl ether with sodamide in liquid ammonia, the thiol being subsequently added.

When ethoxyethyne was added to a solution of free thiol in liquid ammonia, doubtless containing $RS^-NH_4^+$, a nucleophilic addition occurred too, but this method was not satisfactory for all thiols. t.Butylmercaptan and thiophenol failed to give the expected products in reasonable yields.

Nucleophilic addition of a second thiolate ion was found to be impossible. Addition to I of a second molecule thiol by a radical mechanism using free thiol was easy.

$$CH_2=C(OC_2H_5)(SC_2H_5) + C_2H_5SH \rightarrow C_2H_5SCH_2CH(OC_2H_5)SC_2H_5$$

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An *electrophilic addition* of thiols to ethoxyethyne under the catalytic influence of acids as H_2SO_4, SO_2 or BF_3-etherate, which was expected to produce 1,1-disubstituted ethenes, could not be achieved; the product of the radical addition was obtained instead.

Chapter II* deals with autoxidation of the mono-additionproducts described in chapter I. The reactions with oxygen (1-3 atm. pressure), occurring relatively easily, can be summarised in the following equations. Autoxidation reactions of some related products were studied too.

$$C_2H_5OCH{=}CHSR \rightarrow \begin{matrix} C_2H_5O \\ \\ RS \end{matrix}\!\!\diagdown\!\!\diagup CH\text{-}CHO;\ HCO_2C_2H_5 \text{ and polymers.}$$

$$R = C_2H_5,\ C_3H_7,\ -CH_2C_6H_5,\ -C_6H_4\text{-p.}CH_3.$$

$$C_2H_5OCH{=}C(CH_3)SC_2H_5 \rightarrow CH_3{-}CO{-}CH(OC_2H_5)SC_2H_5;$$
$$HCO_2C_2H_5;\ CH_3COSC_2H_5 \text{ and polymers.}$$

$$CH_2{=}C(OC_2H_5)SR \rightarrow RS{-}CH_2{-}CO_2C_2H_5;\ CH_2O;\ CH_3CO_2C_2H_5.$$
$$R = C_2H_5,\ C_3H_7,\ -CH_2C_6H_5.$$

$$C_2H_5OCH{=}CHOC_2H_5 \rightarrow HCO_2C_2H_5 \text{ and polymers.}$$

$$C_2H_5OCH{=}CHCl \rightarrow HCO_2C_2H_5 + [HCOCl]$$
$$\downarrow$$
$$CO + HCl$$

$$HCl + C_2H_5OCH{=}CHCl \rightarrow C_2H_5OCHClCH_2Cl$$

In all oxidations small amounts of ethanol and traces of acetaldehyde and thiol were also formed along with various unidentified low boiling products.

The autoxidation of 1,2-bis-ethylthioethene occurred very slowly and did not give products wich could be identified apart from small amounts of diethyldisulfide.

In general it was found that quantities up to 1.2 atoms of oxygen per mole were consumed. In oxidations of 1,2-disubstituted ethenes the *cis* isomers appeared to react more readily than the corresponding *trans* isomers. The oxidations could be inhibited by small amounts of thymol. Below the compounds are listed in order of decreasing reactivity:

$$CH_2{=}C(OC_2H_5)SR\,(R = C_2H_5,\ C_3H_7) \gg C_2H_5OCH{=}CHSR\ (R = C_2H_5,\ C_3H_7,$$
$$CH_2C_6H_5, p\text{-}CH_3C_6H_4) \gg C_2H_5OCH{=}C(CH_3)SC_2H_5 \approx C_2H_5OC(CH_3){=}CHSC_2H_5 >$$
$$> C_2H_5OCH{=}CHOC_2H_5 > C_2H_5OCH{=}CHCl > CH_2{=}C(OC_2H_5)SCH_2C_6H_5 \gg$$
$$\gg C_2H_5SCH{=}CHSC_2H_5$$

* To be published in Rec. trav. chim.

Generally during these oxidations three reaction types occur:

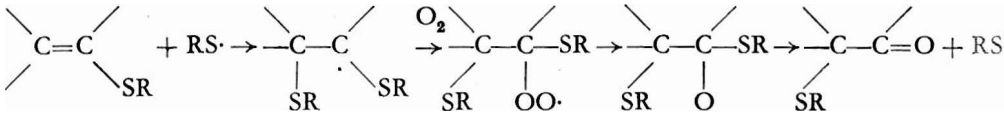
a) an oxidation reaction with uptake of one atom of oxygen per mole accompanied by what is formally a 1.2 shift of the SR grouping (the shift does not occur actually, see mechanism below).

b) fission of the carbon carbon double bond with uptake of one mole of oxygen per mole giving two carbonyl compounds.

c) formation of polymeric, non distillable, materials (only from compounds of the type -S-C=C-O-).

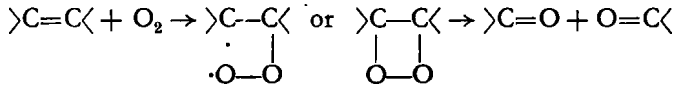
The polymers mentioned gave glyoxal on acid hydrolysis and, when prepared from propene derivatives, methylglyoxal.

The following chain mechanism is proposed to explain reaction a)



The intermediate peroxyradical is probably also involved in reactions leading to b) and c). (See scheme on page 60).

A direct reaction between oxygen and starting material could also account for b).



In chapter III the most important features of the autoxidation of unsaturated halogen compounds are reviewed. These reactions bear much resemblance to the autoxidations of the unsaturated thioethers covered in chapter II, as is apparent from the reaction schemes on page 100-102.

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